

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-171261

(43)Date of publication of application : 09.07.1993

(51)Int.Cl.

C21D 1/70

C09D 1/00

C21D 9/00

C23F 11/00

(21)Application number : 03-353039

(71)Applicant : NKK CORP

MITSUMARU KASEI KOGYO KK

(22)Date of filing : 18.12.1991

(72)Inventor : SASAKI TAKETO

KUWATA MASAYOSHI

MUTA KIYOSHI

IDETA TATATOMI

MATSUURA TOSHIAKI

TERUI KUNIHIRO

YAMAGUCHI AKIRA

(54) ANTIOXIDANT COATING MATERIAL FOR STEEL MATERIAL

(57)Abstract:

PURPOSE: To effectively prevent oxidation, scale developing and decarbonizing and to further improve the detachment of the scale irrespective of difference of kind of the steel and the operational method.

CONSTITUTION: Total 100% of this antioxidant coating material is composed of 5-36wt.% ceramic base material of one or more kinds among silicon carbide, stabilized zirconia, alumina and boron nitride, 15-45wt.% sintering accelerator of one or more kinds among silicon nitride, boron carbide, yttria, manganese dioxide, synthetic mica, magnesium oxide, aluminum nitride and magnesia, 15-70wt.% assistant of one or more kinds among silicic anhydride, chromium oxide, iron oxide, ferric oxide, alumina and calcia, 5-20wt.% binder of one or more kinds among sodium aluminate, low m.p. glass, colloidal silica and alumina sol, 2-4wt.% film reinforcing material of potassium titanate fiber and 2-12wt.% product stabilizer of one or more kinds among sodium citrate, sodium polyacrylate, ammonium oxalate and hydroxyn ethane diphosphine acid.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] Silicon carbide, fully stabilized zirconia, an alumina, and the ceramic base material that consists of one or more sorts in boron nitride, Silicon nitride, boron carbide, yttria, a manganese dioxide, synthetic mica, a magnesium oxide, nitriding aluminum, and the sintering accelerator that consists of one or more sorts in a magnesia, A silicic acid anhydride, chrome oxide, an iron oxide, ferric oxide, an alumina, and assistant ** that consists of one or more sorts in calcia, Aluminum acid soda, low melting glass, colloidal silica, and the binder that consists of one or more sorts in alumina sol, The paint film reinforcing materials who consist of a potassium titanate fiber, and citric-acid soda, sodium polyacrylate, It is the antioxidizing coating for steel which consists of a product stabilizer which consists of one or more sorts in oxalic acid ammonia and hydroxyine ethane diphosphonic acid. said ceramic base material: -- 5 - 36 % of the weight, and said sintering acceleration material -- :5-45 % of the weight -- said -- assistant -- **:15-70 % of the weight and said binder: -- by said product stabilizer:2-12% of the weight of presentation 5 - 20 % of the weight, and said paint film reinforcing materials:2-4% of the weight And the antioxidizing coating for steel whose sum total of the component is 100 % of the weight.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] When the grain boundary oxidation decarbonization which poses a quality top problem is suppressed, and it can moreover exfoliate easily before rolling and a scale is generated, this invention relates to the antioxidizing coating for steel which makes descaling easy, while it is applied to steel, especially slab slab and prevents oxidation of that front face, and generating of the scale in the high-temperature-oxidation ambient atmosphere in a heating furnace.

[0002]

[Description of the Prior Art] Although slab slab is set to a heating furnace or a soaking pit, it heats and rolls out at 1100 degrees C - 1300 degrees C and it becomes a product, the furnace operation conditions of this heating furnace are determined by the operating condition of the construction material of slab, size, and a circumference facility.

[0003] By the way, it sets in the slab slab in such a heating furnace or a soaking pit, The problem that the quality deteriorated remarkably by no less than 0.6 - 1.2% of the weight of the scale generating even the case of plain steel with a slab thickness of 250mm from the time amount in **** or the effect of temperature, there being a problem that the yield gets worse, and the oxidation on a grain boundary especially occurring [temperature] above 1150 degrees C with steel of a certain kind, and causing decarbonization in high-carbon steel etc. had arisen.

[0004] The heating-at-high-temperature approach by the steel surface protective cover by the heating-at-high-temperature approach ** thin griddle by spreading of the high-temperature-oxidation prevention coating containing the metal or mineral salt of a ** silica system, magnesia system refractories, and the low melting point was widely performed as a technique of preventing above oxidation and scale generating of slab slab, and decarbonization conventionally.

[0005]

[Problem(s) to be Solved by the Invention] However, there were the following problems in these conventional approach.

** a silica system, magnesia system refractories, the metal of the low melting point, or the high-temperature-oxidation prevention coating containing mineral salt is the difference in the steel type of content slab, such as Cu, nickel, and Cr, and the difference in the operation approach of continuous system or a batch type heating furnace, and oxidation, scale generating prevention, and its detachability are inadequate -- etc. -- there is a fault.

** Since it becomes indirect heating with needing a great effort for anchoring to steel, the steel surface protective cover approach by the thin griddle has a fault, such as becoming the aggravation factor of the material unit of a heating furnace fuel.

[0006] This invention was originated in view of the above point of the conventional technique, and the object tends to offer the antioxidizing coating for steel which has improved the detachability of a scale more while preventing oxidation, scale generating, and decarbonization effectively irrespective of the difference in a steel type, or the difference in the operation approach.

[0007]

[Means for Solving the Problem] this invention persons came to complete this invention, as a result of considering various component selections and component presentations especially in order to obtain an antioxidizing coating which intercepts a furnace atmosphere and steel effectively.

[0008] this invention persons as a ceramic base material Namely, silicon carbide, fully stabilized zirconia, Among an alumina and boron nitride, as one or more sorts and sintering acceleration material Silicon nitride, Boron carbide, yttria, a manganese dioxide, synthetic mica, a magnesium oxide, Among nitriding aluminum and a

magnesia, as one or more sorts and assistant ** A silicic acid anhydride, chrome oxide, Among ferrous oxide, red iron oxide, an alumina, and calcia, as one or more sorts and a binder Aluminum acid soda, Among low melting glass, colloidal silica, and alumina sol, as a potassium titanate fiber and a product stabilizer as one or more sorts and paint film reinforcing materials Citric-acid soda, While choosing one or more sorts in sodium polyacrylate, oxalic acid ammonia, and hydroxyine ethane diphosphonic acid the presentation -- said ceramic base material: -- 5 - 36 % of the weight, and said sintering acceleration material: -- five to 45% of the weight Said assistant **: by considering as 15 - 70 % of the weight, said binder: 5-20 % of the weight, said paint film reinforcing materials: 2-4 % of the weight, and said product stabilizer: 2-12 % of the weight, and making the sum total of the component into 100 % of the weight It comes to complete this invention which prevents oxidization, scale generating, and decarbonization effectively, and can perform descaling easily.

[0009] Hereafter, the detail of this invention is explained.

[0010] Although the ceramics is used as a base material of a component, this ceramics needs to have high thermal resistance and that component presentation needs to be 5 - 36% of the weight of the range. At less than 5 % of the weight, formation of a precise paint film was not obtained, and contact of oxidizing atmosphere gas increased in steel, thermal conductivity fell further, and since consumption of heating energy increased and it became an energy loss, 5 % of the weight was made into the minimum. On the other hand, although the effectiveness as a base material is eternal even if it exceeds 36 % of the weight, a precise paint film is not formed and the early object is not reached. For this reason, 36% was made into the upper limit. In addition, silicon carbide is a thing with a mean particle diameter of 44micro in the impalpable powder or alpha-sic which was excellent in the degree of sintering with a mean particle diameter of 0.5micro or less with beta-sic, and what raises the thermal conductivity nature of a paint film is more desirable. The thing of an alumina with the high and degree of sintering of alpha crystal (3-4micro) which has small contraction and which moreover has a fluidity to water is desirable.

[0011] the thing to which the acceleration of sintering of the ceramic base material and binder which sinter sintering acceleration material in 300 degrees C - 800 degrees C is made to perform -- it is -- mixing of a coating -- training -- a field is hard, and raises the adhesion reinforcement on the front face of steel, and the duty which brings about a precise paint film is achieved. if less than 5 % of the weight -- a sintering condition -- bad -- mixing -- training -- the reinforcement between paint films in an object falls, it becomes the pervasion region of an oxidizing atmosphere, and a steel front face gets worse. For this reason, 5 % of the weight was made into the minimum. On the other hand, if it exceeds 45 % of the weight, the precise paint film of a ceramic base material will not be formed, but it will deviate from the early object. For this reason, 45 % of the weight was made into the upper limit.

[0012] Assistant ** aims at assistance of effectiveness, such as improvement in the heat transfer rate of a sintering formation paint film, reinforcement of a degree of sintering, improvement of warm strength, and hydration reaction prevention of a coating, to each component in a coating. At less than 5 % of the weight, when 70 % of the weight is exceeded in scale control, a difficulty is looked at by the decarbonization prevention effectiveness and detachability. For this reason, while making 5 % of the weight into the minimum, 70 % of the weight was made into the upper limit.

[0013] While a binder makes association of the ceramic base material of a component stabilize, it is necessary to raise adhesion with steel, and 5 - 20% of the weight of the range needs to have the component presentation. less than 5 % of the weight -- mixing -- training -- an object is hard and the adhesion force to a steel side is not acquired. For this reason, 5 % of the weight was made into the minimum. On the other hand, when 20 % of the weight is exceeded, detachability is spoiled remarkably. For this reason, 20 % of the weight was made into the upper limit.

[0014] Paint film reinforcing materials raise the warm strength of a paint film, and it aims at making almost equal the amount of thermal expansion of a coating paint film to the base material (slab) to apply. Moreover, since it is a ceramic fiber with the very high rate of infrared radiation (emissivity), there is work by which improvement in the thermal conductance by radiation of a formation paint film is achieved. At less than 2 % of the weight, a formation paint film cannot follow the thermal expansion of a base material, and a crack may arise. For this reason, 2 % of the weight was made into the minimum. Moreover, since it was 2 - 4 % of the weight, more remarkable one as effectiveness made 4 % of the weight the upper limit as a more desirable value. In addition, as for this paint film reinforcing materials, it is desirable to use the thing of with diameters 10-30micro and a die length [100-500micro] tabular fiber.

[0015] A product stabilizer acquires the stable distributed condition of you TINGU material (liquid), and has the

work which carries out an adjustment operation of the potential decision ion concentration which enlarges the condensation prevention and surface potential by dissolved polyvalent metal ion like calcium²⁺ and aluminum³⁺ which are contained in the coating concerned, and Fe³⁺ ion. At less than 2 % of the weight, if the thickening state of aggregation of a coating happens and 12 % of the weight is exceeded, a modulation will be caused to a binder component and baking paint film reinforcement will be spoiled remarkably. For this reason, while making 2 % of the weight into the minimum, 12 % of the weight was made into the upper limit.

[0016] Since thermal conductivity does not fall by the thin paint film neutrally, the coating of this invention attains many results, such as saving resources, workability, energy saving, and an environmental ambient atmosphere improvement, while raising the reinforcement between paint films which used the ceramics as the base material as mentioned above, and the adhesion reinforcement to a metal material front face.

[0017] If paint film thickness is explained here, in less than 50micro, to heating in a heating furnace, the effectiveness of the scale generating prevention by oxidation of steel and control will be low, and the scale with dramatically bad detachability which adhered firmly will be generated in special high-class steel (Cu, nickel, Cr content). As this to paint film thickness becomes thick, scale generating prevention and depressor effect become higher.

[0018] However, if it exceeds 500micro, heating heat transfer will get worse, and it will be obliged to modification of the heat pattern of furnace operation, or extension of heating time, and will not be desirable. Moreover, the reinforcement of the paint film at the time of slab handling has the problem of being proportional to paint film thickness mostly, is judged synthetically, and serves as range where paint film thickness (200-400micro) is desirable. In addition, when about 10 - 15% of the weight of water is mixed in an applicable constituent in applying the constituent of this invention on steel, paint workability improves notably.

[0019]

[Example] Hereafter, the example of this invention is explained concretely.

[0020] It evaluated under the conditions which show the examples 1-15 of this invention below per three points of scale depressor effect, scale detachability, and the decarbonization prevention effectiveness.

Test coupon: High-carbon steel, tool steel, structural steel worker alloy steel, particular application steel, plain steel in-furnace time: 5 hours (maximum-temperature soaking-time 3 hours)

maximum-temperature: -- the inside of 1200-degree-C **10-degree-C furnace -- O₂ %: 1-5% -- film thickness -- : --

350micro [0021] Next, the component of examples 1-15 and its presentation are shown. Among the component, silicon carbide ** is a thing with a mean particle diameter of 44micro in alpha-sic about the impalpable powder which excelled [** / especially / silicon carbide] in the degree of sintering with a mean particle diameter of 0.5micro or less by beta-sic, and alumina ** used the thing of low-temperature-sintering nature with a mean particle diameter of 0.5micro for what the degree of sintering of alpha crystal (3-4micro) is high, and alumina ** of contraction is [what] small, and moreover has a fluidity to water in some which raise the thermal conductivity nature of a paint film.

[0022] O Example 1 Ceramic base material Silicon carbide **: 3 % of the weight Silicon carbide **: 2 % of the weight Sintering acceleration material Silicon nitride : 6 % of the weight Boron carbide : 3 % of the weight Ytria : 2 % of the weight A manganese dioxide : 8-% of the weight synthetic mica : 6 % of the weight Assistant ** Silicic acid anhydride : 25 % of the weight chromic oxide: 15 % of the weight Ferrous oxide : 10 % of the weight Binder Sodium aluminate : 5 % of the weight Low melting glass : 3 % of the weight Paint film reinforcing materials Potassium titanate fiber : 2-% of the weight product stabilizer Citric-acid soda: 8-% of the weight sodium

polyacrylate : 2 % of the weight [0023] O Example 2 Ceramic base material Silicon carbide **: 4 % of the weight Silicon carbide **: 2 % of the weight Fully stabilized zirconia : 3 % of the weight Alumina **: 5 % of the weight Alumina **: 4 % of the weight Sintering acceleration material silicon nitride : 1-% of the weight boron carbide : 1 % of the weight Ytria : 2-% of the weight manganese dioxide : 1 % of the weight Assistant ** Silicic acid anhydride : [20 % of the weight] Chrome oxide: 8 % of the weight Iron oxide : 15 % of the weight A binder Aluminum acid soda : 15-% of the weight low melting glass : 5 % of the weight Paint film reinforcing materials Potassium titanate fiber : 4 % of the weight Product stabilizer Citric-acid soda : 5 % of the weight Sodium

polyacrylate : 5 % of the weight [0024] O Example 3 Ceramic base material Silicon carbide **: 4 % of the weight Silicon carbide **: 2 % of the weight Fully stabilized zirconia : 3 % of the weight Alumina **: 5 % of the weight Alumina **: 4 % of the weight Sintering acceleration material silicon nitride : 10 % of the weight Boron carbide : 8 % of the weight Ytria : 2-% of the weight manganese dioxide : 12 % of the weight Synthetic mica : 12 % of the weight Assistant ** Silicic acid anhydride : 9 % of the weight Chrome oxide : 3 % of the weight Ferrous oxide: 3

[illegible]

material Silicon carbide **: 5 % of the weight Fully stabilized zirconia : 3 % of the weight Alumina **: 6 % of the weight Sintering acceleration material Silicon nitride : 7 % of the weight A manganese dioxide : 6 % of the weight Magnesia: 3-% of the weight boron carbide : 3 % of the weight Ytria : 1-% of the weight assistant ** Silicic acid anhydride : 9 % of the weight ferric oxide : 10-% of the weight alumina : 6 % of the weight Calcia: 10-% of the weight chromic oxide : 14 % of the weight Binder Colloidal silica : 8-% of the weight low melting glass : 2 % of the weight Paint film reinforcing materials ***** ** firefly epsilon**^*** ** ***** **

***** therefore*****◇ ** ***** ***** ***** ***** ***** (5)

***** [0033] O Example 12 Ceramic base material Silicon carbide **: 12 % of the weight Silicon carbide **: 7 % of the weight Fully stabilized zirconia : 6 % of the weight Alumina **: 10 % of the weight Sintering acceleration material Silicon nitride : 8 % of the weight A manganese dioxide : 6 % of the weight Magnesia: 6 % of the weight Boron carbide : 3 % of the weight Ytria : 2 % of the weight Assistant **

Silicic acid anhydride: 5 % of the weight Ferric oxide : 3-% of the weight alumina : 2 % of the weight Calcia: 4-% of the weight chromic oxide: 2-% of the weight binder Alumina sol: 7 % of the weight Low melting glass : 3 % of the weight Paint film reinforcing materials Potassium titanate fiber : 4-% of the weight product stabilizer Oxalic acid ammonia : 4 % of the weight sodium polyacrylate : 4 % of the weight Hydroxyine ethane diphosphonic acid: 2 % of the weight [0034] O Example 13 Ceramic base material Silicon carbide **: 5 % of the weight Fully

stabilized zirconia : 4 % of the weight Alumina **: 5 % of the weight Sintering acceleration material Silicon nitride : 2 % of the weight A manganese dioxide : 3 % of the weight Magnesia: 5-% of the weight yttria : 2 % of the weight Assistant ** Silicic acid anhydride : [14 % of the weight] Ferric oxide: 7 % of the weight Alumina : 9 % of the weight Calcia : 17 % of the weight Chrome oxide : 9 % of the weight Binder Colloidal silica : 3-% of the weight alumina sol : 3 % of the weight Low melting glass : 2 % of the weight paint film reinforcing materials

Potassium titanate fiber : 3 % of the weight Product stabilizer Oxalic acid ammonia : 3 % of the weight Sodium polyacrylate : 2 % of the weight Hydroxyine ethane diphosphonic acid: 2 % of the weight [0035] O Example 14 Ceramic base material Silicon carbide **: 4 % of the weight Silicon carbide **: 1 % of the weight Fully

stabilized zirconia : 2 % of the weight Alumina **: 3 % of the weight Sintering acceleration material Silicon nitride : 1 % of the weight A manganese dioxide : 3 % of the weight magnesia: 5 % of the weight Ytria : 1-% of the weight assistant ** Silicic acid anhydride : 17 % of the weight Ferric oxide : 5-% of the weight alumina : 10 % of the weight Calcia : 21-% of the weight chromic oxide: 7 % of the weight Binder Colloidal silica : 3-% of the weight alumina sol : 2 % of the weight Low melting glass : 1 % of the weight Paint film reinforcing materials

Potassium titanate fiber : 4 % of the weight Product stabilizer Oxalic acid ammonia : 5 % of the weight Sodium polyacrylate : 3 % of the weight Hydroxyine ethane diphosphonic acid: 2 % of the weight [0036] O Example 15 Ceramic base material Silicon carbide **: 2 % of the weight Alumina **: 3 % of the weight Sintering

acceleration material Silicon nitride : 2 % of the weight Manganese dioxide : ***** ◇ **

***** | ***** ** * -VI ** [***** ** horizontal ***** O ***** **

***** ** ***** ** *****◇ ** ***** O ***** ** *****

***** ***** ** ***** ***** ***** _ ***** ** *****

firefly epsilon**^*** ** ***** ** ***** therefore*****◇ **

***** ***** ***** ***** (5) ***** ***** [0037]

moreover, three round head of the content shown below as an antioxidizing coating of the conventional technique - formation -- it compared with HOKUN H-17 (trademark) by industrial incorporated company. Let this be the example 1 of a comparison. In addition, conditions presupposed that it is completely the same as that of this example.

[0038] O Example of comparison 1 silicon carbide : 18 Weight % silicon nitride : 1.5-% of the weight alumina : 22 Weight % silicic acid anhydride : 10 Weight % boron nitride : 2 Weight % alumina sol : 13 Weight % low melting glass : 3 Weight % chromite sand : 15.5-% of the weight potassium titanate fiber : 3 Weight %Fe powder: 9

Weight % manganese dioxide : 3 Weight % [0039] Assessment of the above this examples 1-15 and the example 1 of a comparison is shown in a table 1 - a table 3. Assessment of scale depressor effect and a table 2 show assessment of the detachability of an antioxidizing coating, a table 3 shows assessment of the decarbonization prevention effectiveness, respectively, and, as for a table 1, the notation in a table shows the superiority or inferiority of assessment. The content is shown in a table 4. In addition, it was estimated that the Vickers hardness decrement in 1mm ***** of surfaces was also for the decarbonization prevention effectiveness of a table 3.

[0040]

[A table 1]

スケール抑制効果

試験材	実 施 例															比較例
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
高炭素鋼	○	◎	◎	◎	◎	◎	◎	◎	◎	○	◎	◎	◎	◎	○	△
工具鋼	○	◎	◎	◎	◎	◎	◎	◎	○	○	○	◎	◎	◎	○	△
構造用合金鋼	○	○	○	◎	◎	◎	○	◎	○	○	○	◎	○	◎	○	○
特殊用途鋼	○	○	○	○	◎	○	○	◎	○	○	○	◎	○	○	○	○
普通鋼	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	○	○

[0041]

[A table 2]

酸化防止塗料の剥離性

試験材	実 施 例															比較例
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
高炭素鋼	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	○
工具鋼	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	○
構造用合金鋼	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	△
特殊用途鋼	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	○
普通鋼	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎

[0042]

[A table 3]

脱炭防止効果

試験材	実 施 例															比較例
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
高炭素鋼	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
工具鋼	○	◎	◎	◎	◎	◎	◎	◎	○	○	◎	◎	◎	◎	○	△
構造用合金鋼	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
特殊用途鋼	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
普通鋼	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

[0043]

[A table 4]

記号	表1. スケール抑制効果	表2. 塗料の剥離性	表3. 脱炭防止効果
◎	スケール発生なし	100%剥離	$\Delta H_v = 0 \sim 20$ 未満
○	5%未満	99~80%	20~50未満
△	5~15%	79~60%	50~100未満
×	15%超え	59%以下	100超え

[0044] In this example, it turned out with any steel of a class that generating of a scale is excellent in less than 5% and scale depressor effect so that more clearly than a table 1. Especially, in examples 5, 8, and 12, it excelled, so that there was no generating of a scale.

[0045] Moreover, detachability with scale exfoliation altogether very as remarkable [this example] also in the steel of which kind as 100% was accepted so that more clearly than a table 2.

[0046] Furthermore, it turned out that the decarbonization prevention effectiveness excels the conventional thing in this example so that more clearly than a table 3.

[0047]

[Effect of the Invention] Exfoliation of a scale can also be ensured while being able to prevent oxidation of steel, scale generating, and decarbonization effectively irrespective of the difference in a steel type, or the difference in the operation approach according to the antioxidizing coating for steel concerning this invention, as explained above.

[Translation done.]